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Toward Quantitative Prediction of Stereospecificity of Metallocene-Based Catalysts for α-Olefin Polymerization

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The *qualitative* relationship between the local structure of the *ansa*-metallocene catalysts and the resulting polypropene can readily be addressed through e.g. simple symmetry-rules[1] and molecular mechanics calculations[2], whereas the question of to what extent the tacticity of the polymer actually can be *quantitatively* predicted through independent means has not received much attention.

We are currently investigating to what extent combined approaches may contribute to the accuracy of such predictions,[3,4] and we have started out by taking the simplest possible approach: energies of four different (diastereomeric) transition states of propene insertion into the zirconium-polymer bond are obtained using molecular mechanics (MM) geometry optimizations utilizing a frozen central geometry (termed aggregate) taken from a density functional theory (DFT) calculation.

To enable a quantitative comparison with experiment, the energy of the diastereomeric models of the transition state are converted to so-called pentad intensities as obtained from ^{13}C-NMR spectra of the polymer. From the pentad distribution it is possible to extract information about the configuration of five neighboring methyl groups along the polypropene backbone. Through Maxwell-Boltzmann statistics the calculated MM energies are converted to probabilities for obtaining each diastereomer, and in turn, to probabilities for sequences of such diastereomers. The intensity of a given pentad is finally obtained by considering all possible five-membered sequences contributing to that pentad.

For isopropylidene-bridged zirconocene catalysts such as [{^{i}Pr(3-X-CpFlu)}ZrR]$^+$ (X=H, Me, Et, ^{i}Pr, ^{t}Bu; Cp=cyclopentadienyl, Flu=fluorenyl), the computed pentad distributions generally follow the observed ones below 30–50°C, with typical RMS deviations for the 10 pentads of a given catalyst remaining within a few percentage-points. Above 30–50°C the observed decrease in specificity is generally underestimated by the calculations, indicating the onset of competing isomerization reactions at elevated temperatures.

The computational results[4] indicate that the molecular structure of the catalyst cation is even more decisive to the polymer microstructure than previously assumed. The refined description of the catalyst–polymer relationship, especially the introduction of the effects of temperature, has also brought about new mechanistic insight, in particular regarding the role of intermediate chain migration (back-skip)[3]. Finally, accurate prediction of polymer microstructure from independent means also seems to be a strategy of potential value for catalyst development and improvement.

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